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# Early transition metal catalyzed-hydroboration of alkenes

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## Abstract

A variety of well-defined early transition metal complexes were tested as catalyst for the hydroboration of 1-hexene using catecholborane as boration agent. The variations applied concerned both metal (Y, La, Ti, Zr) and spectator ligand system (bis(cyclopentadienyl), bis(pentamethylcyclopentadienyl), bis(benzamidinate), cyclopentadienyl-benzamidinate, cyclopentadienyl-aryloxy, and cyclopentadienyl-amido). Most systems proved to be catalytically active (anti-Markovnikov regioselectivity, side reactions negligible), but the observed activity was in all cases lower than reported for  $\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$  [1]. Inactivation of the catalyst by catecholborane or Lewis base-metal complex induced disproportionation of catecholborane appeared to compete effectively with the catalytic conversion, thus leading to inefficient catalytic performance and complicated product mixtures. Systems with bidentate, cyclopentadienyl ligands with a pending anionic (aryloxy, amido) function showed a moderate catalytic activity but excellent catalyst stability and open up interesting perspectives for further exploration.

**Keywords:** Alternative ligand systems; Early transition metals; Homogeneous catalysis; Hydroboration

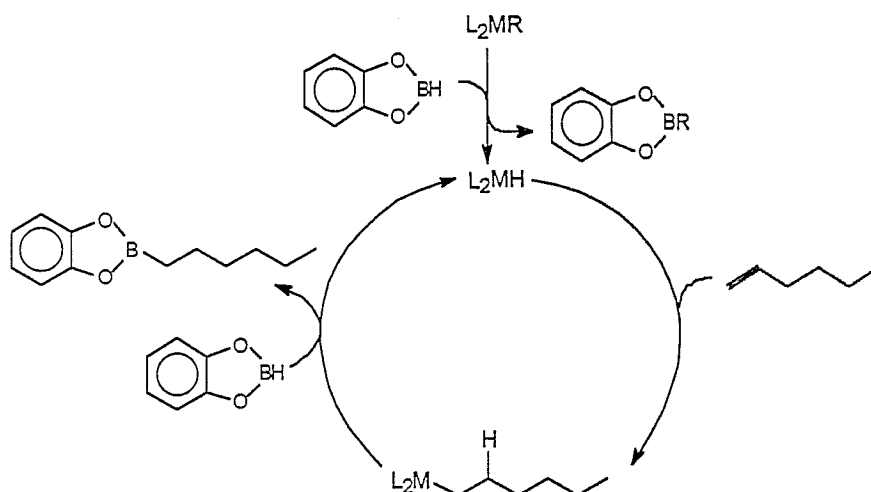
## 1. Introduction

For organic synthesis, hydroboration of alkenes forms an interesting synthetic methodology since the products can conveniently be transformed into alcohols [2], amines [3] or halides [4]. The application has greatly been enhanced by rhodium-catalyzed processes which afford good chemoselectivity [5], regioselectivity (usually Markovnikov) [6–9], diastereoselectivity [10,11], enantioselectivity [12–15] and high reaction rates, although relatively large amounts ( $\approx 5\%$ ) of hydrogenated alkenes and diborated products [16,17] somewhat limit the usefulness of this catalytic system. Recently, efficient and selective organolanthanide-catalyzed hydrobora-

tion of alkenes using catecholborane,  $\text{HB}(1,2\text{-O}_2\text{C}_6\text{H}_4)$ , was reported by Harrison and Marks [1]. Mechanistically the catalytic reaction follows a different path (regioselectivity anti-Markovnikov) than for rhodium while side reactions (diboration, isomerization, hydrogenation) are negligible. The catalytic cycle proposed is given in Scheme 1; the key step is generation of a metal-hydride from the catalyst precursor, which is followed by insertion of an olefin, while after that  $\sigma$ -bond metathesis to form the hydroboration product takes place and the catalyst is regenerated [1].

Essential for a successful catalytic system seems to be coordinative unsaturation (16 or lower electron system) and facile (re)generation of a M–H bond. Our group has available a wide

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Scheme 1. Proposed mechanism of organolanthanide-catalyzed alkene hydroboration.

range of well-characterized early transition metal complexes, with various auxiliary ligand systems and which meet, in principle, the requirements for catalytic hydroboration viz. the compounds are coordinatively and electronically unsaturated, form metal–hydrides easily and contain polar bonds in order to favor a partially charged four-centered transition state. It was decided to explore their potential as catalyst in the hydroboration of 1-hexene and compare the results with those published for the  $\text{Cp}^*_2\text{LnR}$  systems ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{Ln} = \text{La}, \text{Sm}$ ;  $\text{R} = \text{H}, \text{CH}(\text{SiMe}_3)_2$  [1].

## 2. Experimental

### 2.1. General details

All manipulations were performed under nitrogen using glove box techniques. Benzene- $d_6$  was distilled from Na/K alloy and stored under nitrogen. NMR spectra were recorded on a Varian Gemini 200 ( $^1\text{H}$ , 200 MHz) or on a Varian VXR-300 ( $^1\text{H}$ , 300 MHz;  $^{11}\text{B}$ , 96.2 MHz;  $^{13}\text{C}$ , 75.4 MHz).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced internally using residual solvent resonances relative to tetramethylsilane.  $^{11}\text{B}$ -NMR spectra were referenced externally to  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . Catecholborane (Aldrich) was distilled under reduced pressure and stored under nitrogen. 1-Hexene was

filtered over alumina (neutral, Merck), distilled from calcium hydride and stored under nitrogen. Reagent purity was ascertained by  $^1\text{H}$ -NMR spectroscopy or GC. GC analyses were performed on a Hewlett Packard 5890A apparatus equipped with a HP-1 30 m  $\times$  0.53 mm capillary column. GC–MS measurements were performed on a Ribermag R10-10C equipped with a CP Sil 5 CB 25 m  $\times$  0.32 mm capillary column.

### 2.2. Synthesis of catalyst precursors

The synthesis of the following early transition metal complexes have been published or will be reported elsewhere:  $\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$  (1) [18],  $\text{Cp}^*_2\text{YCH}(\text{SiMe}_3)_2$  (2) [19],  $\text{Cp}^*_2\text{YMe}(\text{THF})$  (3) [20],  $(\text{Cp}^*_2\text{YH})_2$  (4) [21],  $\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2$  (5) ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) [22],  $\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2 \cdot \text{Et}_2\text{O}$  (6) [22],  $\text{Cp}^*_2\text{TiMe}_2$  (7) [23,24],  $\text{Cp}^*_2\text{ZrMe}_2$  (8) [23,24],  $\text{Cp}_2\text{TiMe}_2$  (9) [25],  $\text{Cp}_2\text{ZrMe}_2$  (10) [25],  $\text{Cp}^*_2\text{Ti}(\text{allyl})$  (11) (allyl =  $\eta^3\text{-C}_3\text{H}_5$ ) [26],  $\text{Cp}_2\text{Ti}(\text{allyl})$  (12) [26],  $\{[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YH}\}_2$  (13) [27],  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YCH}(\text{SiMe}_3)_2$  (14) [27],  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YCH}_2\text{Ph} \cdot \text{THF}$  (15) [28],  $[\text{C}_6\text{H}_5\text{C}(\text{NCMe}_3)_2]_2\text{YCH}(\text{SiMe}_3)_2$  (16) [28],  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_3\text{La}$  (17) [29],  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{TiMe}_2$  (18) [28],  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{ZrMe}_2$  (19) [28],

$\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{TiMe}_2$  (20) [28],  
 $\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{TiNp}$  (Np =  
 $\text{CH}_2\text{C}(\text{CH}_3)_3$ ) (21) [28],  
 $\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{Zr}(\text{CH}_2\text{Ph})_2$  (22) [30],  
 $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{Ti}(\text{allyl})$  (23) [31],  
 $\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{Ti}(\text{allyl})$  (24) [28],  
 $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{Zr}(\text{BH}_4)_2$  (25) [32],  
 $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{Zr}(\text{CH}_2\text{Ph})_2$  (26) [32],  
 $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{TiMe}_2$  (27) [33],  
 $[\text{C}_5\text{Me}_4(2\text{-O})(6\text{-OMe})\text{C}_6\text{H}_3]\text{TiNp}_2$  (28) [34],  
 $[\text{C}_5\text{Me}_4(2\text{-O})(6\text{-OMe})\text{C}_6\text{H}_3]\text{Ti}(\text{allyl})$  (29)  
 [34].

### 2.3. General procedure for the catalyzed hydroboration of alkenes

A 5-mm NMR tube equipped with a Teflon needle valve was charged with 0.30 mmol of olefin, 0.60 mmol of catecholborane, 0.3 ml benzene- $d_6$ , and 10  $\mu\text{mol}$  of catalyst precursor (1–29). Progress of the reaction was monitored following the intensity of the olefinic resonances in the  $^1\text{H}$  NMR spectrum. The alkylborane ester formed was identified by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy. After all 1-hexene had been consumed, the mixture was quenched with 0.25 ml 3 M NaOH and 0.50 ml 30%  $\text{H}_2\text{O}_2$  and warmed to  $50^\circ\text{C}$  for 3 h. The

organic layer was separated and analyzed with  $^1\text{H}$ -NMR spectroscopy, GC and GC–MS.

### 2.4. Reactions of catecholborane with the precatalyst

A 5-mm NMR tube, equipped with a Teflon needle valve, was charged with 10  $\mu\text{mol}$  of catalyst precursor (1–29), 0.3 ml benzene- $d_6$ , and 50  $\mu\text{mol}$  of catecholborane. The resulting mixture was characterized spectroscopically by  $^1\text{H}$ ,  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR.

### 2.5. Determination of gross activity

The conversion of 1-hexene to the alkylborane ester was determined after one hour reaction by  $^1\text{H}$ -NMR spectroscopy (Table 1). The gross activity was calculated by dividing the amount of formed hydroboration product by the amount of precatalyst started with. Repeated runs for a number of complexes (1, 2, 3, 5, 11, 13, 18, 19, 20 and 23) proved to be reproducible (within 5–10%), indicating that uncontrolled, trivial inactivation (air, water) of the catalyst was not likely.

Table 1

Observed conversions after 1 h reaction time (mol product per mol catalyst per hour) for the hydroboration of 1-hexene with selected early transition metal complexes

$\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$ (1)	60	$[\text{C}_6\text{H}_5\text{C}(\text{NCMe}_3)_2]_2\text{YCH}(\text{SiMe}_3)_2$ (16)	2.0 <sup>a</sup>
$\text{Cp}^*_2\text{YCH}(\text{SiMe}_3)_2$ (2)	1.3	$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_3\text{La}$ (17)	0.6
$\text{Cp}^*_2\text{YMe}(\text{THF})$ (3)	1.1	$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{TiMe}_2$ (18)	1.5 <sup>a</sup>
$(\text{Cp}^*_2\text{YH})_2$ (4)	1.3	$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{ZrMe}_2$ (19)	5.0 <sup>a</sup>
$\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2$ (5)	20 <sup>a</sup>	$\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{TiMe}_2$ (20)	2.2 <sup>a</sup>
$\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2\cdot\text{Et}_2\text{O}$ (6)	15 <sup>a,b</sup>	$\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{TiNp}$ (21)	1.8 <sup>a</sup>
$\text{Cp}^*_2\text{TiMe}_2$ (7)	0.2 <sup>c</sup>	$\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{Zr}(\text{CH}_2\text{Ph})_2$ (22)	4.8 <sup>a</sup>
$\text{Cp}^*_2\text{ZrMe}_2$ (8)	0.2 <sup>c</sup>	$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{Ti}(\text{allyl})$ (23)	5.0 <sup>a</sup>
$\text{Cp}_2\text{TiMe}_2$ (9)	4.7 <sup>a,b</sup>	$\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{Ti}(\text{allyl})$ (24)	3.6 <sup>a</sup>
$\text{Cp}_2\text{ZrMe}_2$ (10)	2.0 <sup>a,b</sup>	$[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{Zr}(\text{BH}_4)_2$ (25)	1.4
$\text{Cp}^*_2\text{Ti}(\text{allyl})$ (11)	0.1 <sup>c</sup>	$[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{Zr}(\text{CH}_2\text{Ph})_2$ (26)	0.2 <sup>c</sup>
$\text{Cp}_2\text{Ti}(\text{allyl})$ (12)	0.2 <sup>c</sup>	$[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{TiMe}_2$ (27)	1.8
$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YH}$ (13)	5.0 <sup>a</sup>	$[\text{C}_5\text{Me}_4(2\text{-O})(6\text{-OMe})\text{C}_6\text{H}_3]\text{TiNp}_2$ (28)	0.7
$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YCH}(\text{SiMe}_3)_2$ (14)	4.4 <sup>a</sup>	$[\text{C}_5\text{Me}_4(2\text{-O})(6\text{-OMe})\text{C}_6\text{H}_3]\text{Ti}(\text{allyl})$ (29)	0.9
$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YCH}_2\text{Ph}\cdot\text{THF}$ (15)	1.6 <sup>a,b</sup>		

<sup>a</sup> Rapid catalyst deactivation was observed.

<sup>b</sup> Decomposition of  $\text{HB}(1,2\text{-O}_2\text{C}_6\text{H}_4)$  to  $\text{B}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)_3$  took place, see [39].

<sup>c</sup> Reaction rate comparable with the uncatalyzed hydroboration of 1-hexene.

Table 2

Estimated turnover frequencies (mol hydroboration product per mol catalyst per hour) for the hydroboration of 1-hexene for selected early transition metal complexes

$\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$ (1)	130
$\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2$ (5)	50
$\{[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YH}\}_2$ (13)	7.0
$\text{Cp}[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]\text{TiMe}_2$ (20)	8.0
$[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{Ti}(\text{allyl})$ (23)	14

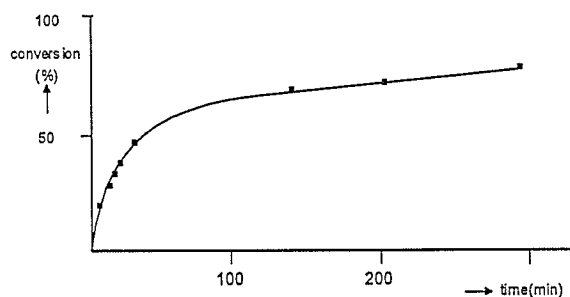


Fig. 1. Conversion plot for the hydroboration of 1-hexene with  $\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2$  (5) as catalyst.

## 2.6. Determination of turnover frequency

For a number of selected catalytic systems (e.g. 1, 5, 13, 20 and 23) an estimate of the turnover frequency could be made from the observed linear part of the conversion curve (Table 2, Fig. 1). For others rapid catalyst deactivation or catalyzed decomposition of catecholborane made this impossible.

## 3. Results and discussion

We have concentrated on a model system using catecholborane and 1-hexene (Scheme 2) earlier explored by Harrison and Marks [1]. The early transition metal complexes to be tested were selected on the basis of their analogy with the  $\text{Cp}^*_2\text{LnR}$  systems used by Marks with variations in the auxiliary ligand system, the metal and the nature of the active ligand. The  $\text{Cp}^*_2$  group has been replaced either by  $\text{Cp}_2$ , Cp-aryloxide, Cp-

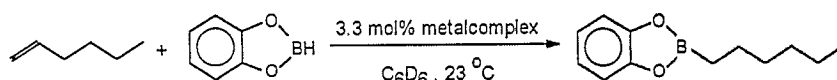
amide, Cp-benzamidinate or bis(benzamidinate). Also several metals (Y, La, Ti, Zr) and active ligands (hydride or carbyl) have been used. All complexes studied meet the criteria for possible catalytic activity, they are coordinatively unsaturated (10–16 electron systems), and have M–H or M–C bonds which can easily be transformed into M–H bonds by the catecholborane added.

### 3.1. General aspects

The general features of the observed conversion plots are those of an S-curve like frequently observed in catalysis (Fig. 1). After initiation (i.e., formation of the catalyst from the precursor and catecholborane), a period of maximal catalytic activity starts, which lasts till inactivation of the catalyst becomes notable whereupon the catalysis gradually stops and at last only the uncatalyzed reaction proceeds after complete inactivation of the catalyst has occurred. For most complexes catalyst formation is complete within 5 minutes at room temperature. For precursors with M–R bonds, catecholborane–R was detected by NMR spectroscopy. In general, the metal–hydride generated during this initiation step reacted very quickly either to give the catalytic reaction or deactivation. Attempts to identify the products formed in the latter by comparing the NMR spectra with published data, were only possible for a limited number of the catalysts tested. Further plans for experiments to solve this problem were abandoned on the basis of the experience of Marks et al. [35] in this area.

For 2, 9, 10, and 17, no fast reaction with catecholborane was observed. In some cases catalytic inactivity due to a rapid side reaction of catecholborane took place; this aspect will be discussed further on.

All catalytic runs, except those using  $\text{Cp}_2\text{TiMe}_2$  (9) and  $\text{Cp}_2\text{ZrMe}_2$  (10), proceeded with high regioselectivity (anti-Markovnikov >99%) and



Scheme 2. Reaction of catecholborane with 1-hexene catalyzed by early transition metal complexes.

low substrate hydrogenation (<2%)<sup>1</sup>. In the presence of group 4 compounds **9** and **10** the regioselectivity (anti-Markovnikov) decreased to 93% and 95% respectively. Table 1 shows the observed conversions for the systems tested.

### 3.2. Bis(cyclopentadienyl) systems

First, we tested  $\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$  (**1**) to check our system and compare it with the work by Harrison and Marks [1]. Indeed, high activity and selectivity were observed and the results are in agreement with those reported.  $\text{Cp}^*_2\text{YCH}(\text{SiMe}_3)_2$  (**2**) turned out to be much less active, which is in line with the observation that in other catalytic systems e.g. olefin hydrogenation and ethylene polymerization lanthanide metals show quite a large spread in activity which can be related to the steric aspects of the various metal centers [18,36]. The fact that the smaller metal here also gives the slower catalyst indicates that the hydroboration system is more related to ethylene polymerization than to hydrogenation of olefins [36]. The rate determining step seems to be formation of the hydroboration product and regeneration of the catalyst and the reduction of space around the metal center when going from La to Y apparently raises the concerted  $\sigma$ -bond metathetical transition state. For **2**, the initiation step is very slow as formation of the hydride ( $\text{Cp}^*_2\text{YH}$ )<sub>2</sub> was not observed. Instead a slow loss of  $\text{Cp}^*$  ligands from yttrium was found. Other permethyltrocene complexes  $\text{Cp}^*_2\text{YMe}(\text{THF})$  (**3**), and ( $\text{Cp}^*_2\text{YH}$ )<sub>2</sub> (**4**) proved to be moderately active as well and give, grosso modo, the same results as **2**. The view that the final step in the cycle is rate determining is supported by the observation that for the dimeric hydride **4** combination of the reagents leads to immediate loss of the characteristic hydride resonances indicating a rapid dissociation into monomers and consequent fast hexene insertion (this step is well-documented cf. [37,38]) while the catalytic activity is the same

as found for the other  $\text{Cp}^*_2\text{Y}$  compounds **2** and **3**. The sterically more accessible yttrium complexes  $\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2$  (**5**) and  $\text{Cp}_2\text{YCH}(\text{SiMe}_3)_2 \cdot \text{Et}_2\text{O}$  (**6**) showed a marked increase in activity, although it did not reach the value found for **1**. Unfortunately, rapid, concurrent catalyst deactivation was observed for these systems, which limits the overall catalytic performance of the complexes. Remarkable is the significant decomposition of catecholborane to  $(1,2\text{-O}_2\text{C}_6\text{H}_4)_3\text{B}_2$  [39] in the presence of diethyl ether complex **6**. This was not found for **5**, which instead reacted rapidly with catecholborane to form a complex mixture of boron compounds. On the basis of  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy we could identify  $(1,2\text{-O}_2\text{C}_6\text{H}_4)\text{BCH}(\text{SiMe}_3)_2$ , but two signals ( $^{11}\text{B}\{^1\text{H}\}$  NMR,  $\delta=8.4$  (singlet) and  $-26.3$  (quartet,  $J_{\text{B-H}}=90$  Hz) ppm) remain unassigned. Efforts to isolate these products were unsuccessful and identification of these products was not possible.

The  $d^0$ , 16 electron systems  $\text{Cp}^*_2\text{TiMe}_2$  (**7**) and  $\text{Cp}^*_2\text{ZrMe}_2$  (**8**) showed no catalytic activity at all. For  $\text{Cp}_2\text{TiMe}_2$  (**9**), neither reaction nor catalytic activity was observed at first, then transient low activity followed, probably because of formation of catalytically active thermolysis or photolysis products [40].  $\text{Cp}_2\text{ZrMe}_2$  (**10**) itself seems not catalytically active at all. The compound however reacts with catecholborane to give  $\text{B}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)_3$ ,  $\text{Cp}_2\text{Zr}(\text{BH}_4)_2$  [41,42], the methyl-boron ester and  $\text{BH}_3$ , all of which were identified by NMR spectroscopy. Remarkable is that for both **9** and **10** small amounts of the Markovnikov product are formed (7% and 5% respectively). This could be explained by reaction of 1-hexene with  $\text{BH}_3$  [43] (present according to  $^{11}\text{B}$ -NMR spectroscopy), like observed for other catalytic systems [35,44].<sup>2</sup>

The  $d^1$ , 15 electron systems  $\text{Cp}^*_2\text{Ti}(\text{allyl})$  (**11**) and  $\text{Cp}_2\text{Ti}(\text{allyl})$  (**12**) were not catalytically active at all.  $^1\text{H}$ -NMR spectroscopy showed that

<sup>1</sup> The uncatalyzed hydroboration of 1-alkenes shows anti-Markovnikov regioselectivity.

<sup>2</sup> For less unsaturated lanthanide complexes and more heavily substituted alkenes Harrison and Marks observed decomposition of catecholborane to give mixtures in which  $\text{B}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)_3$  and  $\text{BR}_3$  proved to be present [35].

the allylborane ester was formed quickly and it therefore is reasonable to assume that the titanium–hydride necessary to start the catalytic cycle has been generated. Olefin insertion should be possible then [45], but closing the catalytic cycle is too difficult and catalyst deactivation competes effectively. Considering the decrease in size of metal going from yttrium to titanium it is expected that for the latter a higher activation energy will be encountered in the last step and that catalytic activity will be very low. The systems were not studied in detail because the catalysts and some of the products are paramagnetic.

### 3.3. Alternative ligand systems

Our group is exploring the chemistry of early transition metal and lanthanide complexes with an alternative coordination environment around the metal center and comparing their properties with known bis(pentamethylcyclopentadienyl) systems. We decided to concentrate on two types of ligands namely benzamidates (Fig. 2) [27] and on bidentate ligands combining a cyclopentadienyl with a pendant anionic (aryloxide or amide) functionality [32,46]. Benzamidate ligands are ‘harder’ Lewis bases than cyclopentadienyl ligands [30]. Therefore the metal-center will be more Lewis acidic, which will influence the metal–alkyl bonding and the transition state of the final  $\sigma$ -bond metathesis step. Although the steric aspects of dish-shaped ( $\text{Cp}$ ,  $\text{Cp}^*$ ) and wedge-shaped (benzamidate) ligands are difficult to assess, a molecular model study of  $\text{Cp}^*_2\text{YR}$ ,  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{YR}$  and  $\text{Cp}_2\text{YR}$  ( $\text{R} = \text{H}$ , alkyl), assuming freely rotating ligands, suggests that the steric bulk of benzamidates is

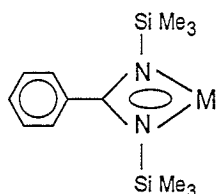


Fig. 2. Benzamidate ligand system.

between that of cyclopentadienyl and permethylcyclopentadienyl [28].

All benzamidate complexes tested (**13–24**) proved to be catalytically active, but the activity is about 1/9–1/18 of that of the lanthanum complex **1**. All runs proceeded with concurrent fast deactivation of the catalyst due to reaction between catecholborane and the benzamidate ligands, probably to give products with B–N bonds. Nevertheless, bis(benzamidate)yttrium systems (**13,14**) showed a catalytic activity substantially higher than the bis(pentamethylcyclopentadienyl)yttrium compounds (**2–4**), but lower than the bis(cyclopentadienyl)yttrium complexes (**5,6**), indicating that a more open metal center increases the rate of reaction. From this it may be anticipated that bis(benzamidate)lanthanum systems will have a much higher hydroboration rate. To test this the synthesis of  $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{LaR}$  complexes was attempted. Unfortunately, only tris(benzamidate)lanthanum (**17**) could be obtained and the planned comparison was not possible. The tris(benzamidate)lanthanum itself was also tested. The complex slowly reacts with catecholborane under transfer of the benzamidate ligands to boron, and the resulting products proved to be slightly catalytically active.

Remarkably, decomposition of catecholborane to  $(1,2\text{-O}_2\text{C}_6\text{H}_4)_3\text{B}_2$  appears to be promoted when Lewis bases (THF and diethyl ether) are present but only in combination with a metal complex (e.g., **6** and **15**). Other decomposition products could not be identified unequivocally.  $\text{BH}_3$ , a likely product, could not be observed, nor its hexene insertion product  $\text{B}(\text{hexyl})_3$  ( $^{11}\text{B}$ -NMR). For the titanium systems **18**, **20** and **21** a dark colored reaction mixture developed, which indicates reduction to low valent titanium species. The catalytic activity of the mixed cyclopentadienyl-benzamidate compounds **20–22** and **24** is comparable with that of the bis-benzamidates (**13–16**, **18–19**), but significantly higher than that of the titanium(III) allyls of **11** and **12**.

In addition to the benzamidate systems, we explored new bidentate ligands which combine a

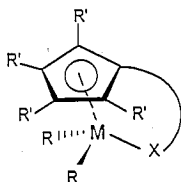


Fig. 3. Bidentate cyclopentadienyl ligand with a pendant 'anionic' ligand X.

cyclopentadienyl with a pendant anionic function X (Fig. 3) [32,46]. Both steric and electronic effects can be tuned here by varying the coordinating group X (X = amide, alkoxide, phosphide, sulfide) and the substituents R' (R' = H, alkyl, silyl, aryl) on the cyclopentadienyl group. Unfortunately so far only group 4 complexes of this class of ligands are available. There is one exception at the moment: Bercaw studied catalytic properties of some related scandium compounds, including polymerization and oligomerization of  $\alpha$ -olefins [47]. The open structure around the metal center suggests less steric hindrance during the catalytic conversions, which should enhance activity for sterically more demanding substrates.

Monomeric zirconium cyclopentadienyl-amide (25–27) and titanium cyclopentadienyl-aryloxide (28,29) complexes proved to be catalytically active, with an activity comparable to other Ti and Zr compounds tested but dramatically less than the lanthanum compound **1**. Apparently, for these systems the reaction rate is decreased by electronic effects, since sterically there is more space available at the metal center. A remarkable feature of these systems is that catecholborane is not decomposed and also that the bidentate cyclopentadienyl 'anionic' ligand system is not attacked. From this point it seems attractive to concentrate on group 3 complexes containing these bifunctional, bidentate ligands since the larger space available there suggests a much higher catalytic activity. Experiments in this area are under way at the moment.

#### 4. Conclusions

Catalytic olefin hydroboration with group 3 and group 4, 10–16 electron organometallic com-

pounds as catalysts strongly depends on the size of the metal and the stabilizing auxiliary ligand system present. For bis (pentamethylcyclopentadienyl) complexes the highest catalytic activity and stability of the catalyst is found for lanthanum, the largest metal. For smaller metal centers (Y, Zr, Ti) catalytic activity is low while catalyst inactivation by transfer of the spectator ligand to the boron hydride reagent is usually fast. Other ligand systems (bis(cyclopentadienyl), bis(benzamidinate) and mixed cyclopentadienyl-benzamidinate) are less effective in stabilizing the catalysts. Bidentate ligand systems based on cyclopentadienyl ligands with pending anionic functions (aryloxo, amido) form stable catalysts. The catalytic performance is moderate but possibly can be improved considerably by using larger metal centers. For this, lanthanides seem the elements of choice.

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